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PROTECTION FROM OXYGEN AND MOISTURE VIA THIN OXIDE BARRIER COATING FOR ORGANIC ELECTRONICS

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ABSTRACT

Protection from oxygen and moisture is crucial for organic light emitting diodes (OLED) used in flexible display applications. The surface coating is an effective way to protect the enclosed functional materials and organic substrates in order to ensure their device functionality. Parylene films, which can be vapor deposited at room temperature, are known as a superior conformal polymeric material. In fact, a few attempts have shown that the parylene can be a good barrier coating for the OLED devices. This polymer film cannot, however, provide a long-term reliability due to nature of the polymer degradation in the presence of oxygen and moisture. In order to compensate such a drawback, we have explored the 'biomimetic' solution processing to deposit the oxide films on the organic substrate. Oxide films can provide a better protection and more robust surface. In this study, polyethylene terephthalate (PET) commonly used for an organic substrate, is deposited with the TiO_2 films with or without the parylene underlying layer. Importantly, the oxide coating is processed at very low temperatures ($< 60°C$) in aqueous solution, so the process can avoid premature failure due to high-temperature processes, and is applicable to organic structures, cheap and environment-friendly. In addition, hermeticity tests are devised to measure the moisture and oxygen permeation. Interfacial structure and mechanical properties of the resultant coatings are tested via scanning electron microscope (SEM), atomic force microscope (AFM), optical microscope (OM) and nanoindentation.

INTRODUCTION

Flexible organic light-emitting display technologies offer many potential advantages, such as very thin profiles, lightweight and robust display systems, and the abilities to flex, curve, conform, roll, and fold the display [1]. However, the extreme sensitivity of organic light emitting diodes (OLEDs) to water vapor and oxygen induced degradation place strong demands for thin, flexible barrier coatings. Simple barrier films, consisting of metal or ceramic oxide layers, were developed and successfully utilized in flexible food packaging applications such as snack and coffee packaging. Substrate roughness and defects intrinsic to these materials, however, limit their barrier performance [2]. Although the requirement for the barrier layer of an OLED display is not well defined, it has been found that long-lived OLEDs need a moisture and oxygen barrier layer which transmits less than 10^{-6} g/m²/day of water vapor and 10^{-5}cm³/m²/day of oxygen.

It has been reported that the multilayer barrier coatings of polymer and inorganic dielectric layer can be more than three orders of magnitude less permeable to water and oxygen than an inorganic single layer [3]. In addition, several groups have reported multilayered barriers consisting of inorganic thin films fabricated by conventional vacuum deposition systems [4-6]. To be a good barrier layer, it should not only be free of pinholes but also have good step coverage. It is also very important for the inorganic barrier deposition process to be compatible with the organic emitting layer beneath.

Given a critical need for reliable, high-performance inorganic barrier coatings, this work adopts the 'biomimetic' processing route to deposit oxide barrier coatings on the polymer substrate. This ceramic barrier layer is overlaid on the polymer layer that ensures a conformal coverage over the organic substrate. In particular, ceramic is processed at very low temperature ($<60°C$) in aqueous solution, so the process is also applicable to OLED structures. It is essential to develop materials and processes that can deposit the protective coating conformally on a non-flat (or curved) surface, and develop reliable testing protocols to accurately characterize them.

In this regard, we explore a bi-layer coating system consisting of the aforementioned materials; i.e., biomimetic

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ceramic (TiO$_2$)/conformal polymer (parylene-C) on a PET substrate for potential use in the OLED devices fabricated through the roll-to-roll (r2r) operation. In order to be used as a barrier coating, the top ceramic layer must possess dense and uniform microstructures. The ability to protect the mounted components and substrates from oxygen moisture permeation and to maintain hermeticity is an immediate goal of this study. Ultimately, the processes will be scaled up to the device level for enabling technologies for the barrier coatings.

The dye penetration test will verify the barrier performance of the coatings on the PET substrate. One possible advantage of the dye test is the ability to visualize coating defect sizes and number densities. In addition, this study is supplemented with AFM and SEM characterizations for monitoring structural evolution of the coatings, and with nanoindentation for assessing their mechanical performance.

EXPERIMENTS

PET films (100 µm thick, McMaster-CARR, NJ) are cut into 2.56"-diameter samples and cleaned by acetone, DI water, and iso-propanol in an ultrasonic bath for 10, 5, and 5 minutes respectively. After drying, the PET substrates were air plasma treated for 5 minutes using RF power of 29.6 W at 200 mtorr (Harrick Plasma, NY). A 100 nm thick parylene-C (poly-chloro-para-xylene) was coated on the PET substrates using vapor deposition system (PDS 2010, Specialty Coating Systems, IN). Deposition of ceramic layer (TiO$_2$) was carried out on the parylene-C through a near-room temperature (<60˚C) aqueous solution process. Detailed process of the ceramic coating can be found in the paper by Zhang et al. [8]. The thickness of the ceramic barrier layer was about 50~200 nm. After ceramic coating, the samples were dried in the desiccator for 24 hours.

For hermeticity testing of the ceramic coated PET films, the dye penetration test was set up as shown in Fig. 1. A solution of fluorescent dye was first poured into the glass bottle, and a 2.56"-diameter PET substrate either coated or bare was inserted between the cap and O-rings. In this way, the dye can only penetrate through the PET substrate to reach a silicon wafer which is placed onto the PET substrate. To accelerate the penetration, the glass beaker containing the glass bottle of dye solution was heated up to 110 ˚C in the oven. After this experiment, the silicon wafer was inspected with a 50X microscope under the polarization mode. The illumination of a UV light with wavelength of 365 nm was also used to verify the penetration of dye solution. Residues of the dye, if any, would be activated by the UV light and easily discerned under the microscope. By counting the number of residue spots of the dye on the silicon substrate, we were able to evaluate the hermetic property of the coated PET, as compared to that of the PET-only substrate.

In order to test mechanical performance of the ceramic coatings, we have used the integrated nanoindenter/AFM system (Triboindenter, Hystron, MN). In addition, film adhesion was characterized with a scratch test using the same nanoindentation system. Microstructures and surface morphologies of the coatings were characterized by various microscope techniques including SEM, AFM and OM.
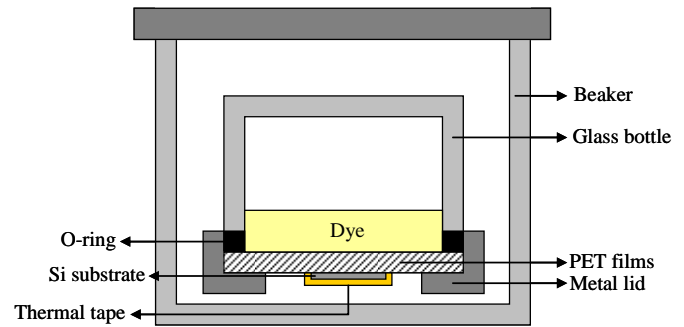

Fig. 1. Schematic of the dye test

RESULTS AND DISCUSSION

1. Microstructures of the PET substrate, Parylene-C, and TiO$_2$ films

As it is reported by many researchers, the surface roughness of thin barrier films causes a permeation of water vapor or oxygen through pinhole defects and nanoscale pores [10-12]. Thus, microstructure evolution of barrier coatings including PET substrate is an important part in this study.

Commercially available thin PET film has shown different surface morphology with its front and back side. The front side has shown much less surface roughness than the back side. We confirmed this observation through an AFM and the barrier films were coated on the surfaces of the front side. A typical AFM image for the front side of PET film is shown in Fig. 2 (a).

Prior to deposition of TiO$_2$ on PET substrates, parylene-C films were coated on PET substrates by using a vapor deposition system. Typical AFM images of top parylene-C coated PET substrate are shown in Fig. 2 (b).
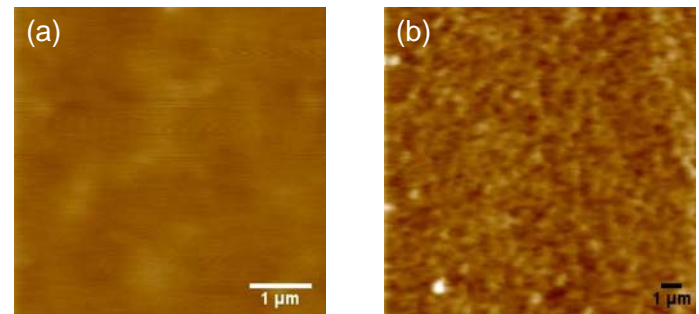

Fig. 2. Typical AFM images of (a) a front side of PET and (b) a parylene-C coated on the plasma treated PET substrate.

The surface roughness of parylene-C film coated on PET substrate shows rougher than the PET surface. It was also

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observed that the air plasma treatment on PET substrate before parylene-C coating did not effectively change its surface morphology.

Since the few nanometers of particle size may cause the permeable defects of water vapor and oxygen in the barrier coating, the evolution of microstructure is the most important part in this study. After parylene-C coating on PET substrates, TiO_2 ceramic layer was coated by using the 'biomimetic' aqueous deposition process at 50~60 ˚C.
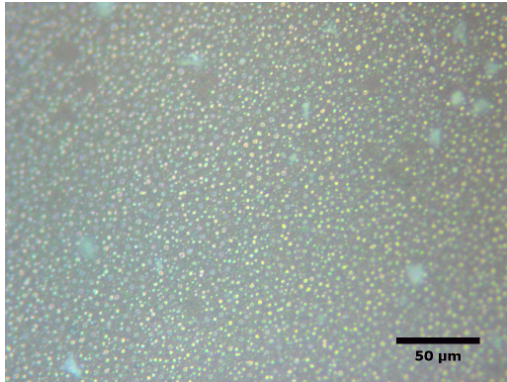

Fig. 3. A typical OM image of TiO_2 film on plasma treated parylene-C underlying plasma treated the front side of PET substrate.

An optical microscope image of TiO_2 films (see Fig. 3) shows that the various sizes of TiO_2 particles successfully formed a ceramic film on the parylene-C coated PET substrates. In Fig. 4, a typical SEM image of TiO_2 microstructure of coating on bare Si substrate is shown for a clear view of microstructure of TiO_2.
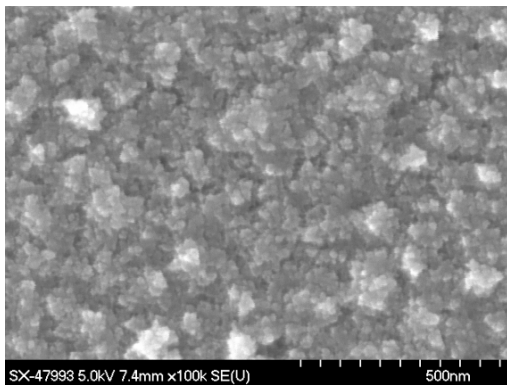

Fig. 4. SEM image showing typical TiO_2 film microstructure.

A microstructure of the TiO_2 coating was also studied by using AFM and is shown in Fig. 5. The size of the particles of TiO_2 is around 200 nm. The size of the particles may need to be reduced less than 50 nm due to the effect of defect size in the barrier coatings. McElvain et al. mentioned that the defect at the barrier coating can be an origin of the water vapor penetration [13, 14].
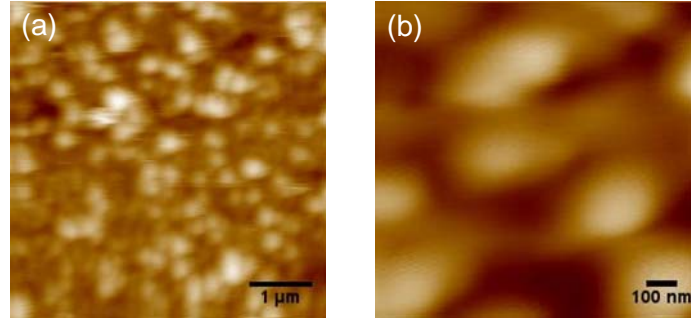

Fig. 5. AFM images of TiO_2 coating on bare PET: (a) lower magnification and (b) higher magnification.

Graff et al. pointed out that the diffusivities of thin, vacuum-deposited inorganic films are many orders of magnitude above those of the bulk materials. This is due to the presence of microscopic defects in the deposited film [5]. The barrier property against the permeability of water vapor and oxygen is not only related by the microscopic structure evolution, but also controlled by the film thickness. Since the film transparency is also an important factor in OLED applications, the film thickness should be considered to ensure the transparency. Therefore, the ceramic coating layer should have fine particles and dense structures with an optimum thickness that satisfies the need for OLEDs.

A series of AFM imaging on TiO_2 films showed the effect of plasma treatment on the underlying layer of parylene-C. The microstructure of TiO_2 films is effectively affected by the underlying layer which is parylene-C. AFM images in Fig. 6 show the effect of plasma treatment on parylene-C prior to TiO_2 ceramic layer deposition. The size of TiO_2 particles with the plasma treatment on parylene-C show much irregular and aggregated shape (see Fig. 6 (a)) than TiO2 on the untreated parylene-C (see Fig. 6 (b)).
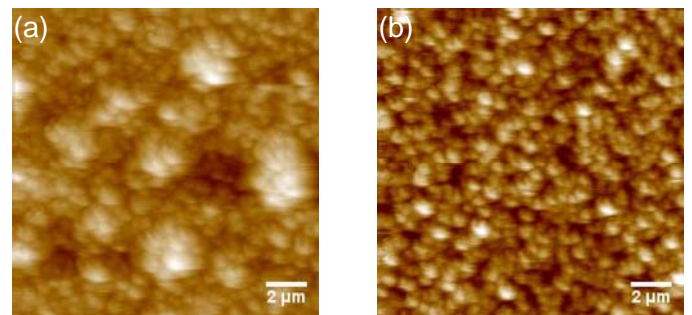

Fig. 6. Typical AFM images of TiO_2 film grown on (a) the plasma treated parylene-C and (b) the untreated parylene-C both on the plasma treated PET substrates.

Plasma treatment usually increases the wettability of polymer surfaces. Parylene-C has also shown the changes of its hydrophobic surface to highly hydrophilic surface after treatment of plasma [15]. The hydrophilic surface of parylene-C presents much more deposition sites which can highly attract the particles to aggregate and make such an island shape as

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shown in Fig. 6 (a). Because the reduction of the surface roughness is one of the primary goals in this study for the OLED applications, the aggregated particles may not helpful for the reduction of surface roughness. In terms of film adhesion, we considered the effect of plasma treatment if the film adhesion can be promoted by applying the plasma treatment.

2. Mechanical Properties of TiO₂, Parylene-C, and PET

In order to measure 'film-only' properties, a commonly used rule of thumb is to limit the indentation depth to less than 10% of the film thickness. However, this rule is not feasible for films that are very thin such that less than 200nm. Based on the Saha and Nix model we have measured 'film-only' properties [16]. Table 1 shows the results for the measurement on each film. Dynamic nanoindentation was used to determine the average intrinsic moduli of the as-deposited TiO₂ film on a Si substrate, parylene-C film on a glass slide, and PET film, respectively.

Table 1. Elastic modulus of the selected coatings for this study.

Films	Elastic modulus (GPa)
TiO₂	19.6 ±1.6 [8]
Parylene-C	3.2 ±0.5 [15]
PET	3.3 ±0.1

3. Interfacial Adhesion of the Coatings: Effect of plasma treatment

In the applications of the flexible OLEDs, the interfacial adhesion among the barrier coating layers, as well as between the barrier coating and the PET substrate, is critical in order to preserve their own functionality to the device. In this study, we first explore the effect of plasma treatments using air as a method to enhance the adhesion strength between a PET substrate and parylene-C interlayer, and also a parylene-C interlayer and a ceramic barrier coating (TiO₂). According to Egitto et al., plasma treatment is one means of modifying polymer surfaces to improve adhesion while maintaining the desirable properties of the bulk materials [17].

Fig. 7 shows AFM images that result of scratch tests using a nanoindentation on the four different samples including parylene-C/PET substrates and TiO₂ films/parylene-C coated PET substrates to investigate the effect of plasma treatment on the underlying films. The ramped normal loading remains such scratch marks as shown in Fig. 7.
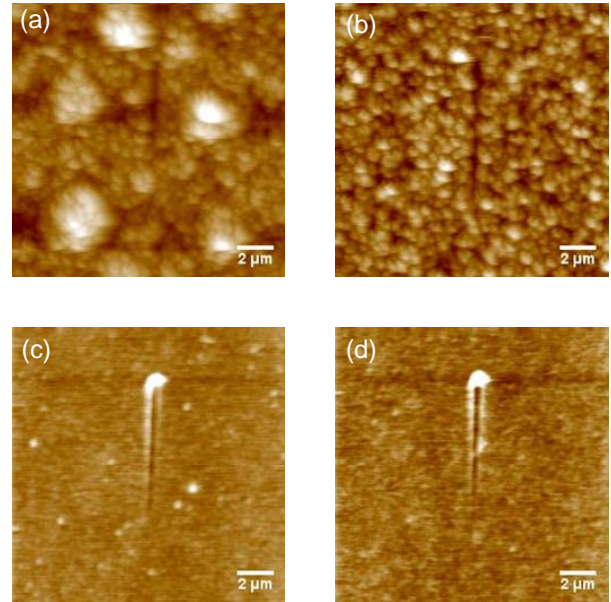

Fig. 7. AFM images of (a) TiO₂ films grown on Parylene-C/PET (both were plasma treated);(b) TiO₂ films grown on Parylene-C/PET (only PET was plasma treated); (c)Parylene-C films grown on the plasma treated PET; (d) Parylene-C films grown on the untreated PET.

A model that relates the critical scratching load to adherence, through the work of adhesion, and is represented by Eq. 1 [18].

$$W_A = \frac{t}{2E_f}\left(\frac{2F_c}{\pi R^2}\right)^2$$

(Eq. 1)

where E_f is elastic moduli of the film, F_c is the critical normal force which can be attained from the scratch tests, R is the radius of the indenter tip (conical shape diamond tip, R=0.764 µm), and t is the film thickness (TiO₂=200nm and Parylene-C=100nm). The elastic modulus of the films was obtained by using a nanoindentation, and the values were shown in Table 1.

In the results, the measured work of adhesion of parylene-C on the PET substrate was slightly lower when the latter was plasma treated than when not treated, as shown in Fig. 8. Since the effect of plasma treatment on polymer surface as an adhesion promoter can be changed and varied when different gases are adopted, we plan to perform more systematic experiments to optimize the condition of plasma treatment on PET substrate prior to deposition of parylene-C.

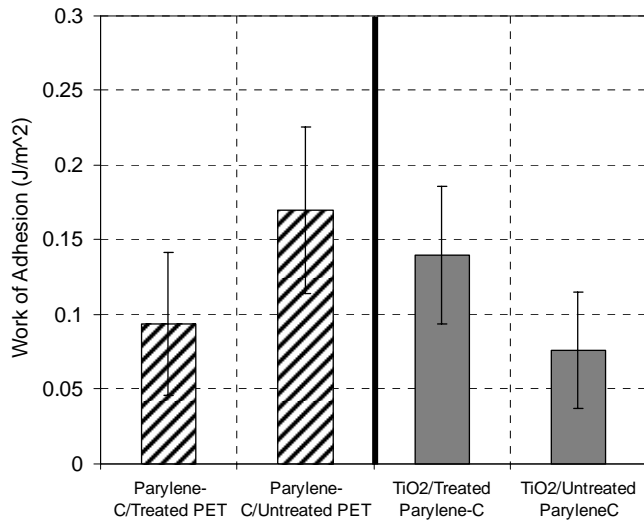4   Copyright © 2007 by ASME

Fig. 8. The results of the scratch tests using a nanoindentation showing the work of adhesion between different samples.

The plasma treatment on the parylene C prior to TiO_2 deposition, however, helped a little for enhancing the adhesion of TiO_2 film on the parylene C. Again, more optimization for plasma treatment, for example, using different gases, will be required to further increase adhesion of the oxide films.

4. Hermeticity of the Barrier Coatings

The dye penetration test results are shown in Fig. 9. The penetrant ratio represents the percentage of dye residue on the Si wafer. Although the barrier coatings have shown better hermeticity (less spots) than the bare PET, there was not much difference among those barrier coatings indicating that the barrier layers including TiO_2 and parylene-C have not reached the goal at this stage. More optimization of the coating processes is under way.
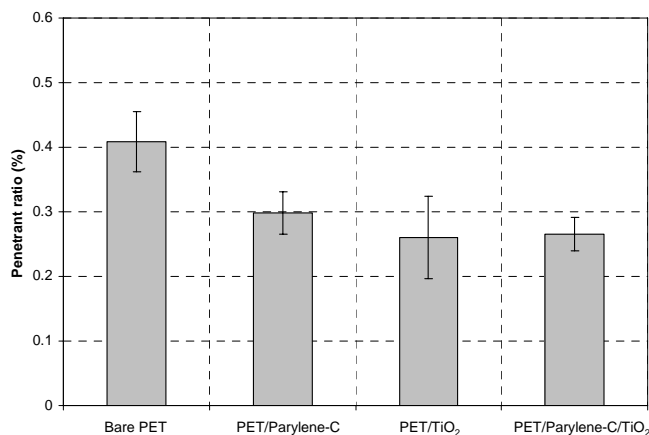

Fig. 9. The dye penetration test results.

CONCLUSION

Titanium oxide (TiO_2) coatings were developed for protecting an OLED device on a flexible substrate from moisture and oxygen. The aqueous solution precursor method via a biomimetic pathway was explored to process oxide coatings at very low temperatures (< 60°C). One objective was to reduce the microscopic defects originated from the surface roughness of the base substrate (PET). The preliminary results show that the TiO_2 coatings are relatively rough when grown on the plasma treated parylene-C/PET substrate; therefore, it will require optimized surface modification of the substrate surface prior to ceramic deposition.

The barrier coatings increased surface properties of the PET ($E \approx 20$ GPa from ≈ 3.3 GPa). In addition, the plasma treatment of the parylene-C makes adhesion of the TiO_2 coatings slightly higher. More improvements in plasma processing are, however, needed for further optimization. From the dye test results, the TiO_2 barrier coatings have shown a potential for improvements of hermeticity of the polymeric PET substrate. Continuous efforts will be directed at further optimizing the performance of the barrier coatings on PET substrate.

ACKNOWLEDGMENTS

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